

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 07-062546

(43)Date of publication of application : 07.03.1995

(51)Int.Cl.

C23C 16/50

C23C 16/26

H01L 21/205

(21)Application number : 05-230768 (71)Applicant : SHINKO ELECTRIC CO LTD

(22)Date of filing : 25.08.1993 (72)Inventor : OKUNO ATSUSHI
NAKAMURA AKIO

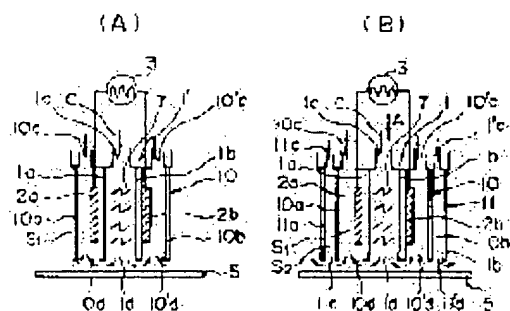
(54) ATMOSPHERIC PLASMA SURFACE TREATING DEVICE

(57)Abstract:

PURPOSE: To provide a plasma surface treating device of a blow off-type capable of preventing the diffusion of the remaining part of the reactive gas blowing off after the end of a treatment and their by-products to the circumference or at least decreasing the amt. of diffusion.

CONSTITUTION: This atm. plasma surface treating device is constituted by providing the outer periphery of a reaction vessel 1 consisting of a dielectric having electrodes 2a, 2b with a box body 10 forming a space to suck blow-off gases, further, providing the outer periphery thereof with an outside box body 11 forming another space on the outer periphery thereof and introducing an inert gas therein so as not to introduce the air into the reaction vessel. The device as another embodiment is constituted by providing the

opposite side of the reaction vessel with respect to the work with a receiving boxy body having an opening slightly larger than a discharge port for the blow-off and treated gases and the inert gas from the outside box when the work is fibrous.



[Detailed Description of the Invention]

[0001]

[Industrial Application] Especially this invention relates to the plasma surface treatment method or the producing-film method by atmospheric pressure glow discharge plasma about a surface treatment method or a method for forming thin film,

and its device.

[0002]

[Description of the Prior Art]In order to form a carbon film, a carbon fluoride film, etc. in the surface of solid materials, such as metal and a ceramic material, Although the mixed gas of inactive gas, such as gas, such as a carbon fluoride system as reactant gas or a hydrocarbon system substance, rare gas, such as helium, argon, and neon, or N_2 , was plasma-ized by the high frequency electric field within the vacuum chamber and coating treatment and thin film forming were performed conventionally, The atmospheric pressure plasma surface treatment method and thin-film-forming method which continue till recent years and need neither a vacuum generator nor a vacuum housing follow on being requested, development is furthered, and technical contents are indicated again. As a typical thing, Japanese Patent Application No. 63-166599 (JP,2-15171,A), Japanese Patent Application No. 61-193934 (JP,63-50478,A), and Japanese Patent Application No. 63-138630 (JP,1-306569,A) are mentioned. Drawing 7 is an outline elevational view showing typically the system for thin film deposition used by these inventions.

The A-A sectional view of drawing 7 is shown in drawing 8.

The structure of this device constitutes the reaction vessel 1 of quadrangle case shape (or barrel) made from a dielectric, To the outside surface of the side attachment walls 1a and 1b (side attachment wall of the right and left in drawing 8) which counter the upper and lower sides or right and left. Attach the electrode 2a and 2b, respectively, connect with the power supply 3 of high frequency high tension, and from the feed port 1c of the reaction vessel 1, Mixed gas with the reactant gas of carbon fluoride systems, such as inactive gas, such as rare gas, such as helium (helium), neon (Ne), or argon (Ar), or N_2 , and CF_4 , or a hydrocarbon system substance, It passes like the arrow C, and it places so that the processed material object 5 may be located under 1d of exit cones of the opposite hand of the feed port 1c and it may move in the direction of the arrow B. If the aforementioned mixed gas is passed and high frequency high tension is impressed to the electrode 2a and 2b with such a structure, Mixed gas plasma-izes by the glow discharge 7, it flows like the arrow D, the radical generated there blows off from 1d of exit cones, and a thin film is formed in refining or the surface for the surface of the processed material object 5.

[0003]

[Problem(s) to be Solved by the Invention]The gas which blew off from the above-mentioned exit cone is diffused in the atmosphere while it processes the surface of a processed material object, but by a reaction with the above-mentioned surface, the by-product as a solid or gas may be generated, and this diffusion gas may pollute the surrounding environment, and may become harmful. Then, it was requested that blow-off gas and a by-product (a solid and gas) were prevented from being spread around, or a diffusing capacity was decreased at least. An object of this invention is to provide the device corresponding to these requests.

[0004]

[Means for Solving the Problem]This invention solved this technical problem by the following means.

(1) Have an electrode and a box for forming space which attracts gas which blows off as emission gas after mixed gas's contacting on the surface of a processed material object from an exit cone around a box-like reaction vessel by the product made from a dielectric and finishing processing is provided, An outer packaging object which forms another space in a periphery of this box is established, and it is made structure which introduces inactive gas, such as Ar and N_2 , from that upper part, and blows off

from a lower end towards a processed material object. When a processed material object is moved, a tip part which counters a processed material object of the aforementioned reaction vessel and a side attachment wall of a box is turned to the vertical medial-axis side side, and is made to incline.

(2) When fibrous in textiles etc. in which a processed material object has breathability, A box which demarcates space which turns inactive gas, such as Ar and N₂, to a processed material object, and blows off around a box-like reaction vessel made from a dielectric which has an electrode is provided, Structure of providing a receiving box object which demarcates another space for gas suction which has a little larger effective area product than sum total blow-off area of reacted mixed gas and inactive gas in a reaction vessel and an opposite hand is used to a processed material object. In the case of a processed material object which moves, it is made into structure according to (1) paragraph.

[0005]

[Function]Although the reactant gas which entered from the feed port is plasma-ized in the case of above (1), and process a processed material object, and it becomes a unconverted gas, subproduction gas, etc., and is drawn in in the space besides a reaction vessel and it is recovered by the external recovery system etc., When the ingredient in the atmosphere mixes in the case of this suction and it influences the aforementioned processing, another outer packaging object for preventing mixing is established, and inactive gas, such as Ar and N₂, is sprayed on a processed material object. Even if the ingredient in the atmosphere mixes, when not influencing processing, an outer packaging object can be omitted. While making the atmosphere hard to involve in by making the tip part which counters a box and the processed material object of the wall of each space incline in the case of the processed material object which moves, recovery of a unconverted gas and inactive gas is ensured. The plasma which was sprayed in the case of the above-mentioned (2) paragraph whose processed material object is a product made from textile materials of breathability processes a processed material object, and the unreacted part and the subproduction gas of gas pass a processed material object, escape from it to an opposite hand the spraying side, are attracted by the receiving box inside of the body, and do not pollute environment. When a processed material object moves, it is the same as that of the case of the aforementioned (1) paragraph.

[0006]

[Example]Drawing of longitudinal section of the 1st example of the atmospheric pressure plasma surface treatment device by this invention is shown in drawing 1 (B), and A view figure of drawing 1 (B) is shown in drawing 2. The same numerals are attached to the same member as drawing 7 and drawing 8 which were shown as advanced technology in these figures. The electrode 2a and 2b are attached to the outside surface of each side walls 1a and 1b on either side with a top view, respectively with the figure of the reaction vessel 1 of the shape of square dielectric box manufacturing, and this electrode 2a and 2b are connected to the power supply 3 of high frequency and high tension. 1 f of peripheral walls before and after the box-like reaction vessel 1 connects between each side walls on either side with the aforementioned each side walls 1a and 1b with a figure, The wrap upper wall 1e is comprised in the upper surface of these one pairs of side attachment walls, and a peripheral wall, the feed port 1c of round hole-like reactant gas is established in this upper wall, the opening of the undersurface is carried out, it serves as 1 d of exit cones of gas, a predetermined distance is maintained under each side walls 1a and 1b which stand straight, and the processed material object 5 is placed horizontally. The

square box 10 is formed by the product made from a dielectric which has the side attachment walls 10a and 10b on the periphery of the reaction vessel 1 so that space S_1 may be formed, . Since the structure of the container itself is almost the same as that of the composition of the aforementioned reaction vessel, omit explanation. They are provided in both sides of the upper bed of the box 10 by the discharge opening 10c and 10'c at the method of both outsides of the feed port 1c of said reaction vessel 1, and the lower end part of the aforementioned side attachment walls 10a and 10b, Only the almost same height as the lower end part of the side attachment walls 1a and 1b of the reaction vessel 1 is located up from the upper surface of the processed material object 5, and 10 d of suction openings and 10'd are formed, respectively between the side attachment wall 1a which is in the same side due to the left and the right in these side attachment walls, and the lower end part of 10a, 1b, and 10b. The square outer packaging object 11 is formed in the periphery of the box 10 by the product made from a conductor so that outside space S_2 may be formed further, They are provided in the right-and-left both outsides of the upper surface by the feed port 11c and 11'c at the method of the outside of the aforementioned discharge opening 10c and 10'c, and, respectively the lower end part of each side walls 11a and 11b, Only the almost same height as the lower end part of the side attachment walls 10a and 10b is located up from the upper surface of the processed material object 5, and 11 d of discharge openings and 11'd are formed between the side attachment wall 10a and each of 11a, 10b, and 11b. Even if the open air mixes, when there is no problem in this processing, the outer packaging object 11 shown in drawing 1 (B) like drawing 1 (A) can be omitted, and it can be considered as the short form reaction vessel 1. [0007]Drawing 3 is drawing of longitudinal section showing the 2nd example for corresponding when the processed object 5 is moved (to left [A figure arrow B]). Although the lower end part of each side walls 31a and 31b of the outer packaging object 31 inclines toward the outside in the inner direction to a vertical axial surface toward the vertical axial surface side, the lower end part of each side walls 21a and 21b of the reaction vessel 21, and each side walls 30a and 30b of the box 30, respectively, Even if the other point is completely the same as that of drawing 1 and the open air mixes, when there is no problem in processing, the outer packaging object 11 can be omitted according to drawing 1 (A).

[0008]Next, an operation of the device of the above 1st and the 2nd example is explained. If drawing 1 and drawing 2 are referred to, the mixed gas of reactant gas, such as CF_4 which entered from the feed port 1c of the reaction vessel 1, and dilution gas, such as helium, It is plasma-ized by the electrode 2a and the glow discharge 7 by the high frequency high tension impressed to 2b, The generated radical blows and comes out of 1d of exit cones, and after processing and reforming the surface of the processed material object 5, it becomes a unconverted gas, subproduction gas, etc., and is collected by 10 d of suction openings, and the recovery container which goes into space S_1 from 10'd, and is not illustrated from the discharge opening 10c and 10'c. inactive gas, such as Ar and N_2 , should be introduced from the feed port 11c of the outer packaging object 11 (31), and 11'c (31c, 31'c), and pass 2nd space S_2 -- the processed material object 5 being sprayed and from 11 d of discharge openings, and 11'd (31 d, 31'd), A part is attracted by 10 d of suction openings, and 10'd (30 d, 30'd), and most is breathed out to the atmosphere of the method of outside, and it intercepts an atmospheric invasion so that processing of the surface treatment of the above [the ingredient in the atmosphere] may not be affected. Since the lower end part of each side attachment wall inclines and is bent toward the vertical medial-axis side side to

the surface of the processed material object 5, respectively when the processed material object 5 is moved in the direction of the arrow B as shown in drawing 3, recovery of raw gas is made much more reliable at the same time it acts so that atmospheric contamination may be prevented.

[0009]Next, with reference to drawing 4, drawing of longitudinal section of the 3rd example corresponding to the case where the processed material object is fibrous in breathability structure like textiles or knitting is shown, and A view figure of drawing 4 is shown in drawing 5. In the device of this example, the same numerals are attached to the same member as drawing 1 and drawing 2, and only a different point is explained. Although the processed material object 25 is breathability fibrous and box 10 the very thing is the same as the case where structures are drawing 1 and drawing 2, 10 f and 10'f are feed ports, and 10 g and 10'g are discharge openings, and to the processed material object 25 in an opposite hand, the gas discharge side. the opening of 12 d of a little larger suction openings than the total area of the gas discharge opening of the reaction vessel 1 and the 1st box 10 was carried out towards the top -- it is flat, and has the square receiving box object 12 for a section, and, as for the receiving box object 12, the discharge opening 12c is formed in the bottom by the product made from a dielectric. The box 10 can be omitted when the atmosphere does not affect processing. Drawing 6 shows the 4th example in case the fibrous processed material object 25 is moved (it is to a left like the arrow B with a figure), The lower end part of each side walls 21a and 21b of the reaction vessel 21 inclines toward the surface of the processed material object 25 like the 2nd example, The lower end part of each side walls 30a and 30b of the box 30 and each side walls 32a and 32b of the downward receiving box object 32 can omit the box 10 like Example 3, when the atmosphere does not affect processing, although it inclines toward the method of outside, respectively.

[0010]An operation of the 3rd above-mentioned example is explained below. Since a unconverted gas, subproduction gas, etc. pass through the processed material object 25 which has breathability unlike the 1st example (refer to drawing 1), It draws in with the receiving box object 12 in the opposite hand of a processing unit, and to the fibrous processed material object 25, penetration of the atmosphere to a treating part makes 10 g of discharge openings of the box 10, and the inactive gas from 10'g blow off, and is prevented. While the end of each side attachment wall is bent and atmospheric contamination is prevented when the processed material object 25 moves in the direction of the arrow B as the 4th example of drawing 6 shows, it is the same as that of the 2nd example (refer to drawing 3) to ensure recovery of gas.

[0011]

[Effect of the Invention]By establishing suction space in the circumference of the exit cone of plasma, in the case of the fibrous object in which a processed material object has breathability, by establishing the receiving box object which forms suction space in an exit cone and an opposite hand to a processed material object, When a processed material object is moved during processing, By making the end face which counters the processed material object of a reaction vessel, a box, an outer packaging object, and a receiving box object incline in the suitable direction, processed subproduction gas and the unconverted gas related to a reaction are emitted into the atmosphere, and having an adverse effect on environment, or the atmosphere flowing in a reaction vessel and having an adverse effect on a reaction is also prevented.

[Claim(s)]

[Claim 1]A box-like or tubed reaction vessel made from a dielectric in which is

provided with the following, a feed port of said mixed gas breaks in the center section of said upper wall, and a crevice between a lower end of said side attachment wall and said processed material object forms a discharge opening of processed gas, One pair of side attachment walls which surround this reaction vessel, are arranged further at a periphery, and form predetermined space between the surfaces of said two electrodes, It has a wrap upper wall for the upper surface of peripheral walls which connect between said each-side-walls order both ends, and these each side walls and peripheral walls, It has the discharge opening of one pair of processed gas which besides ended in an almost symmetrical position to a feed port of mixed gas of said reaction vessel on a wall, A dielectric box-manufacturing object which a lower end of said side attachment wall maintains a predetermined distance to a lower end of said reaction vessel to said processed material object, and is arranged, . It ****, processed gas breathed out from a lower end of said reaction vessel flows through space between a side attachment wall of said box, and a side attachment wall of said reaction vessel up, and it is characterized by passing the aforementioned discharge opening and being collected. Mixed gas of gas, such as a carbon fluoride system as reactant gas or a hydrocarbon system substance, and inactive gas, such as rare gas, such as helium, argon, and neon, or N_2 , is introduced from a one end of one pair of inter-electrode openings which counter under atmospheric pressure and are arranged, With said mixed gas which was sprayed on said inter-electrode another side end on the surface of stillness or a processed material object placed movable, and was plasma-ized by glow discharge under high frequency and high tension. An atmospheric pressure plasma surface treatment device which makes refining or the surface carry out deposit formation of the amorphous carbon film for the surface of said processed material object.

A side attachment wall which said surface treatment device maintained a predetermined interval, countered, and has been arranged in parallel.

One pair of side attachment walls which each of one pair of said electrodes has been arranged on the outside surface, and maintained a crevice between prescribed distances between the surfaces of a processed material object, and have been arranged.

A peripheral wall which connects between said each-side-walls order both ends.

It is a wrap upper wall about the upper surface of these side attachment walls and peripheral walls.

[Claim 2]Have the following and it has the feed port of one pair of inactive gas which broke on this upper wall in a position almost symmetrical with the outside of a discharge opening of one pair of processed gas of said box, To said processed material object, a lower end of said side attachment wall maintains a predetermined distance, and is arranged, Said inactive gas flows through space between an outside surface of each side walls of said box, and an internal surface of an outer packaging object, flows into space between a side attachment wall of said box, and a side attachment wall of said reaction vessel, and is breathed out, and exterior air is prevented from flowing in said reaction vessel, An atmospheric pressure plasma surface treatment device which flows through inside of said box with said processed gas, and is characterized by passing a discharge opening of the upper part and being collected.

One pair of side attachment walls which another outer packaging object made from a conductor is added and provided in a periphery of the; aforementioned box in the atmospheric pressure plasma surface treatment device according to claim 1, and this outer packaging object surrounds said box, are arranged further at a periphery, and form predetermined space between outside surfaces of both side surfaces of said box.

A peripheral wall which connects between front-and-back-ends parts of these each side walls.

It is a wrap upper wall about the upper surface of these each side walls and peripheral walls.

[Claim 3] In the atmospheric pressure plasma surface treatment device according to claim 1 or 2, it is moved in the direction which goes to an electrode of another side from one electrode in said one pair of electrodes, and the; aforementioned processed material object is processed, An atmospheric pressure plasma surface treatment device characterized by a thing of said reaction vessel and a box which a lower end of one pair of side attachment walls inclines in turning inward toward a vertical medial-axis side of one pair of said electrodes, respectively, and a lower end of one pair of side attachment walls of said outer packaging object inclines in extroversion to said vertical medial-axis side.

[Claim 4] Gas characterized by comprising the following which counters under atmospheric pressure and is arranged, such as a one end of one pair of inter-electrode openings to a carbon fluoride system as reactant gas or a hydrocarbon system substance, Mixed gas with inactive gas, such as rare gas, such as helium, argon, and neon, or N_2 , is introduced, With said mixed gas which was sprayed on the surface of a processed material object which stands it still at said inter-electrode another side end, or is placed movable, and was plasma-ized by glow discharge under high frequency and high tension. An atmospheric pressure plasma surface treatment device which makes refining or the surface carry out deposit formation of the amorphous carbon film for the surface of said processed material object.

Said processed material object is a product made from breathability textile materials which can pass, and said mixed gas, such as textiles and knitting, said surface treatment device, One pair of side attachment walls which a predetermined interval is maintained, and it counters, and is arranged in parallel, and each of one pair of said electrodes is arranged on the outside surface, and maintain a crevice between prescribed distances between the upper parts of a processed material object, and are arranged.

A peripheral wall which connects between front-and-back-ends parts of said each side walls.

A box-like or tubed reaction vessel made from a dielectric which it has a wrap upper wall, and a feed port of said mixed gas breaks the upper surface of these each side walls and peripheral walls in the center section of said upper wall, and forms a discharge opening of processed gas in a lower end of said side attachment wall.

One pair of side attachment walls which form a discharge opening of one pair of inactive gas between lower ends of each side attachment wall of said reaction vessel while surrounding this reaction vessel, being arranged further at a periphery and forming predetermined space between the surfaces of said two electrodes, A dielectric box-manufacturing object which has a wrap upper wall and in which a feed port of one pair of inactive gas broke the upper surface of a peripheral wall which connects between said each-side-walls order both ends, and said each side walls and a peripheral wall in an almost symmetrical position to a feed port of mixed gas of said reaction vessel on this upper wall, the opening of a little larger suction opening than the total area of a gas exit cone of a reaction vessel and a box is carried out to an opposite hand of said reaction vessel and a box towards a top to said processed material object -- a section -- a quadrangle -- flat -- a pars basilaris ossis occipitalis -- a discharge opening.

(A)

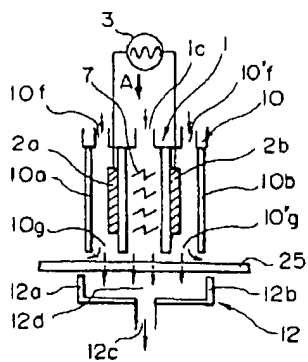
(B)

1a, 1b: 側壁
1c: 導入口
1d: 吹出し口
2a, 2b: 電極
3: 電源
10: 箱体
10a, 10b: 側壁
10c, 10'c: 吐き出し口
10d, 10'd: 吸引口
11: 外箱体
11c, 11'c: 導入口

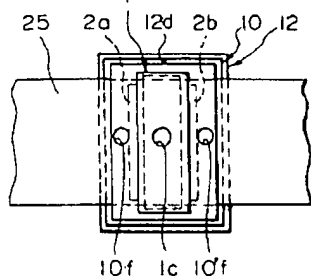
[illegible]

A detailed cross-sectional view of a semiconductor device. It features a substrate 5 at the base. Above it are several layers and regions: a layer 30a with openings 31a; a layer 2a with openings 31b; a layer 30b with openings 31c; and a top layer 21. A central region 30 contains a vertical channel 1d filled with material 31. Other regions include 31c, 21, 30, 31c, 21b, 30b, 31b, 2b, and 5. A voltage source V is connected between regions 31c and 31b. A magnetic field B is indicated by an arrow pointing left.

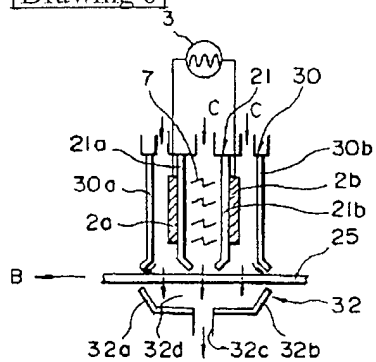
[Drawing 4]



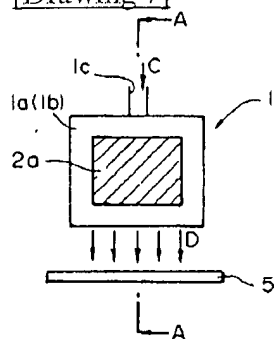
[Drawing 5]



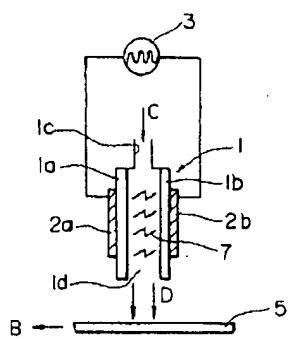
[Drawing 6]



[Drawing 7]



[Drawing 8]



(19)日本国特許庁 (J P)

(12) 公 開 特 許 公 報 (A)

(11)特許出願公開番号

特開平7-62546

(43)公開日 平成7年(1995)3月7日

(51)Int.Cl.⁶

識別記号

庁内整理番号

P I

技術表示箇所

C 2 3 C 16/50

16/26

H 0 1 L 21/205

審査請求 未請求 請求項の数5 F D (全 6 頁)

(21)出願番号 特願平5-230768

(22)出願日 平成5年(1993)8月25日

(71)出願人 000002059

神鋼電機株式会社

東京都中央区日本橋3丁目12番2号

(72)発明者 奥野 敦

三重県伊勢市竹ヶ鼻町100番地 神鋼電機

株式会社伊勢製作所内

(72)発明者 中村 昭生

三重県伊勢市竹ヶ鼻町100番地 神鋼電機

株式会社伊勢製作所内

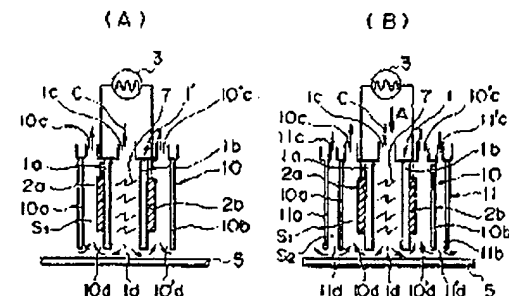
(74)代理人 弁理士 後藤 武夫 (外2名)

(54)【発明の名称】 大気圧プラズマ表面処理装置

(57)【要約】

【目的】 大気圧プラズマ表面処理装置において、処理を終わった後吹き出す反応ガスの残部や副生成物が周囲に拡散するのを防止するか、あるいは少なくとも拡散量を減少させることの可能な吹き出し形のプラズマ表面処理装置を提供する。

【構成】 電極2a、2bを有する誘電体の反応容器1の外周に、吹き出しガスを吸引する空間を形成する箱体10を設け、さらにその外周に別の空間を形成する外箱体11を設けて不活性ガスを導入し大気反応容器内に巻き込まれない構成である。また別の実施例としての装置は、被処理物が繊維状の場合は被処理物に対し反応容器の反対側に、吹き出した処理済みのガスや外箱体からの不活性ガスの吹き出し口よりやや大きい開口を有する受け箱体を設けた構成である。



1a, 1b: 電極

1c: 導入口

1d: 吹き出し口

2a, 2b: 電極

3: 電源

10: 箱体

10a, 10b: 側壁

10c, 10'd: 吹き出し口

10d, 10'd: 吸引口

11: 外箱体

11c, 11'd: 導入口

1

【特許請求の範囲】

【請求項1】 大気圧下に対向して配置される1対の電極間の空隙の一方端から反応ガスとしてのフッ化炭素系あるいは炭化水素系物質などのガスと、ヘリウム、アルゴン、ネオンなどの希ガスまたはN₂等の不活性ガスとの混合ガスが導入され、前記電極間の他方端に静止、または移動可能に置かれる被処理物体の表面に吹き付けられて高周波、高電圧下でのグロー放電によりプラズマ化された前記混合ガスにより、前記被処理物体の表面を改質あるいは表面に例えばアモルファス炭素膜を析出形成させる大気圧プラズマ表面処理装置において、

前記表面処理装置は、
所定の間隔を保って対向して平行に配置された側壁と、その外表面上に前記1対の電極のそれぞれが配置され被処理物体の表面との間に所定距離の隙間を保って配置された1対の側壁と、前記両側壁の前後両端部間を連結する隔壁と、これらの側壁と隔壁の上面を覆う上壁とを有し、前記上壁の中央部に前記混合ガスの導入口が明けられ、前記側壁の下端と前記被処理物体との間の隙間が処理済みガスの吐き出し口を形成する箱状または筒状の誘電体製反応容器と、
この反応容器を囲んでさらに外周に配置されて前記両電極の表面との間に所定の空間を形成する1対の側壁と、前記両側壁の前後両端部間を連結する隔壁と、これらの両側壁と隔壁の上面を覆う上壁とを有し、この上壁上で前記反応容器の混合ガスの導入口に対しほぼ対称の位置に明けられた1対の処理済みガスの吐き出し口を有し、前記側壁の下端は前記被処理物体に対し前記反応容器の下端に対し所定の距離を保って配置される誘電体製箱体と、を有し、前記反応容器の下端から吐き出された処理済みガスが前記箱体の側壁と前記反応容器の側壁との間の空間を上方に流れて前記の吐き出し口を通過し回収されるようになっていないことを特徴とする大気圧プラズマ表面処理装置。

【請求項2】 請求項1記載の大気圧プラズマ表面処理装置において、前記箱体の外周にさらに別の誘電体製外箱体が付加して設けられ、この外箱体は前記箱体を囲んでさらに外周に配置されて前記箱体の両側面の外表面との間に所定の空間を形成する1対の側壁と、これらの両側壁の前後両端部間を連結する隔壁と、これらの両側壁と隔壁の上面を覆う上壁とを有し、この上壁上で前記箱体の1対の処理済みガスの吐き出し口の外側にはほぼ対称の位置に明けられた1対の不活性ガスの導入口を有して、前記側壁の下端は前記被処理物体に対し所定の距離を保って配置され、前記不活性ガスは前記箱体の両側壁の外表面と外箱体の内表面との間の空間を流れて前記箱体の側壁と前記反応容器の側壁との間の空間に流入して吐き出され、外部空気が前記反応容器内に流入するのを防止して、前記処理済みガスとともに前記箱体内を流れその上部の吐き出し口を通過し回収されることを特徴とする

2

大気圧プラズマ表面処理装置。

【請求項3】 請求項1又は2記載の大気圧プラズマ表面処理装置において、前記被処理物体は前記1対の電極中の一方の電極から他方の電極に向かう方向に移動されて処理され、前記反応容器と箱体のそれぞれ1対の側壁の下端は前記1対の電極の垂直中心軸面に向かって内向に傾斜され、前記外箱体の1対の側壁の下端は前記垂直中心軸面に対し外向に傾斜されていることを特徴とする大気圧プラズマ表面処理装置。

【請求項4】 大気圧下に対向して配置される1対の電極間の空隙の一方端から反応ガスとしてのフッ化炭素系あるいは炭化水素系物質などのガスと、ヘリウム、アルゴン、ネオンなどの希ガスまたはN₂等の不活性ガスとの混合ガスが導入され、前記電極間の他方端に静止または移動可能に置かれる被処理物体の表面に吹き付けられて高周波、高電圧下でのグロー放電によりプラズマ化された前記混合ガスにより、前記被処理物体の表面を改質あるいは表面に例えばアモルファス炭素膜を析出形成させる大気圧プラズマ表面処理装置において、
前記被処理物体は繊維物、偏物など前記混合ガスが通過可能な通気性繊維材料製であり、
前記表面処理装置は、

所定の間隔を保って対向して平行に配置されその外表面上に前記1対の電極のそれぞれが配置され被処理物体の上方との間に所定距離の隙間を保って配置される1対の側壁と、前記両側壁の前後両端部間を連結する隔壁と、これらの両側壁と隔壁の上面を覆う上壁とを有し、前記上壁の中央部に前記混合ガスの導入口が明けられ、前記側壁の下端に処理済みガスの吐き出し口を形成する箱状または筒状の誘電体製反応容器と、

この反応容器を囲んでさらに外周に配置され前記両電極の表面との間に所定の空間を形成するとともに前記反応容器のそれぞれの側壁の下端との間に1対の不活性ガスの吐き出し口を形成する1対の側壁と、前記両側壁の前後両端部間を連結する隔壁と、前記両側壁と隔壁の上面を覆う上壁とを有し、この上壁上で前記反応容器の混合ガスの導入口に対しほぼ対称の位置に1対の不活性ガスの導入口が明けられた誘電体製箱体と、

前記被処理物体に対し前記反応容器と箱体の反対側に、反応容器及び箱体のガス吹出し口の合計面積よりもやや大きい吸引口が上に向けて開口され、断面が四角形偏平で底部に吐き出し口が設けられた誘電体製の受箱体と、を含んで成り、

前記反応容器からの処理済みガスが、その外側を流れる前記箱体からの不活性ガスに囲まれてシールされた状態で前記被処理物体を通過して前記受箱体に吸引され回収されることを特徴とする大気圧プラズマ表面処理装置。

【請求項5】 請求項4記載の大気圧プラズマ表面処理装置において、

前記被処理物体は前記1対の電極中の一方の電極から他

方の電極に向かう方向に移動されて処理され、前記反応容器の側壁の下端は前記1対の電極の垂直中心軸面に向かって内向に傾斜され、前記箱体の1対の側壁の下端は前記垂直中心軸面に対し外向に傾斜され、前記受箱体の側壁は前記箱体の1対の側壁の下端よりも広く上向に傾斜されていることを特徴とする大気圧プラズマ表面処理装置。

【発明の詳細な説明】

【0001】

【産業上の利用分野】この発明は表面処理方法あるいは薄膜形成方法とその装置に関し、特に大気圧グロー放電プラズマによるプラズマ表面処理法あるいは製膜法に関する。

【0002】

【従来の技術】金属、セラミック材など固体材料の表面に炭素膜、フッ化炭素膜などを形成するには、従来は反応ガスとしてのフッ化炭素系あるいは炭化水素系物質などのガスとヘリウム、アルゴン、ネオンなどの希ガスまたはN₂等の不活性ガスの混合ガスを真空槽内で高周波電界でプラズマ化してコーティング処理や薄膜形成を行っていたが、近年に至り真空発生装置や真空容器などを必要としない大気圧プラズマ表面処理法や薄膜形成法が要望されるにともない、開発が進められた技術内容が開示されている。代表的なものとして、特願昭63-166599（特開平2-15171）、特願昭61-193934（特開昭63-50478）、特願昭63-138630（特開平1-306569）が挙げられる。図7は、これらの発明で使用される薄膜形成装置を模式的に示す概観立面図であり、図7のA-A断面図を図8に示す。この装置の構造は、誘電体製の四角形箱状（または筒体）の反応容器1を構成して、その上下または左右に対向する側壁1a、1b（図8では左右の側壁）の外表面に、それぞれ電極2a、2bを取り付け、高周波高電圧の電源3に接続し反応容器1の導入口1cから、ヘリウム（He）、ネオン（Ne）またはアルゴン（Ar）などの希ガスまたはN₂等の不活性ガスとCF₄などのフッ化炭素系あるいは炭化水素系物質の反応ガスとの混合ガスを、矢印Cのように流し、導入口1cの反対側の吹き出し口1dの下に被処理物体5を位置させ矢印Bの方向に移動するように置く。このような構造で、前記の混合ガスを流して電極2a、2bに高周波高電圧を印加すると、グロー放電7により混合ガスがプラズマ化し矢印Dのように流れ、そこに生成されるラジカルが吹き出し口1dから吹き出されて被処理物体5の表面が改質あるいは表面に薄膜が形成される。

【0003】

【発明が解決しようとする課題】上記の吹き出し口から吹き出したガスは、被処理物体の表面を処理するとともに、大気中に拡散するが、この拡散ガスは上記の表面との反応によって、固体やガスとしての副生成物が生成さ

れ、周囲の環境を汚染し有害になる場合がある。そこで、吹き出しガスや副生成物（固体及びガス）が周囲に拡散するのを防止するか、或いは少なくとも拡散量を減少させることが要望されていた。本発明はこれらの要望に対応する装置を提供することを目的とする。

【0004】

【課題を解決するための手段】本発明は下記のような手段によりこの課題を解決した。

（1）電極を有し誘電体製で箱状の反応容器の周囲に、混合ガスが吹き出し口から被処理物体の表面に接触して処理を終わった後に排出ガスとして吹き出されるガスを吸引する空間を形成するための箱体を設け、この箱体の外周に別の空間を形成する外箱体を設け、その上部からAr、N₂等の不活性ガスを導入し下端から被処理物体に向け吹き出す構造にする。また、被処理物体が移動される場合には、前記の反応容器と箱体の側壁の被処理物体に対向する先端部を垂直中心軸面側に向け傾斜させる。

（2）被処理物体が通気性を有する織物などの微細状の場合は、電極を有する誘電体製の箱状の反応容器の周囲に、Ar、N₂等の不活性ガスを被処理物体に向けて吹き出す空間を画定する箱体を設け、また被処理物体に対し反応容器と反対側に、反応済み混合ガスと不活性ガスの合計吹き出し面積よりもやや大きい開口面積を有するガス吸引用の別の空間を画定する受箱体を設ける構造にする。移動する被処理物体の場合は（1）項に導ずる構造とする。

【0005】

【作用】上記の（1）の場合、導入口から入った反応ガスはプラズマ化され、被処理物体を処理し未反応ガスと副生成ガス等となって反応容器の外の空間内に吸引され、外部の回収装置などにより回収されるが、この吸引の際に大気中の成分が侵入して前記の処理に影響する場合は、侵入を防止するための別の外箱体を設けてAr、N₂等の不活性ガスが被処理物体に吹き付けられる。大気中の成分が侵入しても処理に影響しない場合には、外箱体を省略することができる。また、移動する被処理物体の場合に、箱体及び各空間の壁の被処理物体に対向する先端部を傾斜させることにより、大気を巻き込み難くするとともに、未反応ガス及び不活性ガスの回収が確実に行われる。被処理物体が通気性の微細材料製である上記（2）項の場合は、吹き付けられたプラズマは被処理物体を処理し、ガスの未反応分や副生成ガスは被処理物体を通過して吹き付け側と反対側に抜けて受箱体内に吸引されて環境を汚染しない。被処理物体が移動する場合は前記（1）項の場合と同様である。

【0006】

【実施例】本発明による大気圧プラズマ表面処理装置の第1実施例の縦断面図を図1（B）に、図1（B）のA矢視図を図2に示す。これらの図において、先行技術として示した図7及び図8と同じ部材には同じ符号を付け

る。平面図で四角形の誘電体製箱状の反応容器1の、図で左右の両側壁1a、1bの外表面には、それぞれ電極2a、2bが取り付けられ、この電極2aと2bは高周波、高電圧の電源3に接続される。箱状の反応容器1は、前記の両側壁1a、1bと、図で左右の両側壁間を連結する前後の隔壁1fと、これら1対の側壁と隔壁の上面を覆う上壁1eとから成り、この上壁には丸穴状の反応ガスの導入口1cが設けられ、下面は開口されてガスの吹き出し口1dとなっていて、直立する両側壁1a、1bの下方には所定の距離を保って被処理物体5が水平に置かれている。反応容器1の外周には、空間S₁を形成するように側壁10a、10bを有する誘電体製の四角形の箱体10が設けられ、容器自体の構造は前記の反応容器の構成とほぼ同一なので説明を省略する。箱体10の上端の左右両側には吹き出し口10c、10'cが前記反応容器1の導入口1cの両外側方に設けられ、前記の側壁10a、10bの下端部は、反応容器1の側壁1a、1bの下端部とはほぼ同じ高さだけ被処理物体5の上面より上方に位置し、これらの側壁中で左、右の関係で同じ側にある側壁1aと10a、1bと10bの下端部の間には、それぞれ、吸引口10dと10'dが形成される。箱体10の外周には、さらに外側の空間S₂を形成するように誘電体製の四角形の外箱体11が設けられ、その上面の左右両側には導入口11cと11'cが、それぞれ、前記の吹き出し口10c、10'cの外側方に設けられ両側壁11aと11bの下端部は、側壁10a、10bの下端部とはほぼ同じ高さだけ被処理物体5の上面より上方に位置し、側壁10aと11a、10bと11bのそれぞれの間には吹き出し口11d、11'dを形成する。外気が侵入してもこの処理に問題がない場合には、図1(A)のように図1(B)に示した外箱体11を省略し簡易型反応容器1とすることができ

る。【0007】図3は、被処理物体5が移動(図では矢印Bのように左方へ)される場合に対応するための第2実施例を示す縦断面図であり、反応容器21の両側壁21a、21bと箱体30の両側壁30a、30bの下端部は、それぞれ、垂直断面側に向かって内方に、外箱体31の両側壁31a、31bの下端部は垂直断面に対して外側に向かって傾斜しているが、それ以外の点は図1と全く同様であり、外気が侵入しても処理に問題がない場合は、図1(A)に準じ外箱体11を省略できる。

【0008】次に上記第1と第2の実施例の装置の作用について説明する。図1及び図2を参照すると、反応容器1の導入口1cから入ったCF₄などの反応ガスとH₂e等の希釈ガスの混合ガスは、電極2a、2bに印加された高周波高電圧によるグロー放電7によりプラズマ化され、生成されたラジカルが吹き出し口1dから吹き出て被処理物体5の表面を処理して改質した後、未反応ガスや、副生成ガス等となって吸引口10d、10'dから

空間S₁に入り吹き出し口10c、10'cから図示しない回収容器に回収される。外箱体11(31)の導入口11c、11'c(31c、31'c)からAr、N₂等の不活性ガスが導入され第2の空間S₂を経て吹き出し口11d、11'd(31d、31'd)から被処理物体5に吹き付けられて、一部は吸引口10d、10'd(30d、30'd)に吸引され、大部分は外方の大気へ吹き出され、大気中の成分が上記の表面改質の処理に影響を与えないように大気の侵入を遮断する。図3に示すように、被処理物体5が矢印Bの方向に移動される場合、各側壁の下端部がそれぞれ被処理物体5の表面に対して垂直中心軸面側に向かって傾斜して曲げられているので、大気の巻き込みを阻止するように作用すると同時に処理ガスの回収を一層確実にする。

【0009】次に図4を参照して、被処理物体が織物または編物のような通気性構造の繊維状になっている場合に対応する第3実施例の縦断面図を示し、図5に図4のA矢視図を示す。この実施例の装置において、図1及び図2と同じ部材には同じ符号を付け、異なる点のみについて説明する。被処理物体25は通気性繊維状で、箱体10自体は構造が図1及び図2の場合と同じであるが、10f、10'fは導入口で、10g、10'gは吹き出し口であり、被処理物体25に対してガス吹き出し側と反対側には、反応容器1及び第1の箱体10のガス吹き出し口の合計面積よりもやや大きい吸引口12dが上に向けて開口された扁平で断面が四角形の受箱体12が備えられ、受箱体12は誘電体製で下側には吹き出し口12cが設けられている。大気が処理に影響を与えない場合は箱体10を省略できる。図6は繊維状の被処理物体25が移動(図で矢印Bのように左方へ)される場合の第4実施例を示し、第2実施例と同様に反応容器21の両側壁21a、21bの下端部は被処理物体25の表面に向かって傾斜し、箱体30の両側壁30a、30bの下端部と下方の受箱体32の両側壁32a、32bはそれぞれ外方へ傾斜しているが大気が処理に影響しない場合は実施例3と同様箱体10を省略できる。

【0010】上記の第3実施例の作用を以下に説明する。第1実施例(図1参照)と異なり、未反応ガスと副生成ガス等が通気性を有する被処理物体25を通り抜けるので、処理装置の反対側にある受箱体12により吸引し、処理部への大気の進入は繊維状の被処理物体25に対し、箱体10の吹き出し口10g、10'gからの不活性ガスを吹き出させて阻止する。図6の第4実施例が示すように、被処理物体25が矢印Bの方向へ移動する場合は、各側壁の端部が曲げられていて、大気の巻き込みが阻止されるとともに、ガスの回収を確実にすることは第2実施例(図3参照)と同様である。

【0011】

【発明の効果】プラズマの吹き出し口の周囲に吸引空間を設けることにより、また被処理物体が通気性を有する織

10

20

30

40

50

繊維状物体の場合は被処理物体に対し吹出し口と反対側に吸引空間を形成する受箱体を設けることにより、また被処理物体が処理の間移動される場合には、反応容器、箱体、外箱体、受箱体の被処理物体に対する端面を適当な方向に傾斜させることにより反応に関与した処理済みの副生成ガスや未反応ガスが大気中に放出され環境に悪影響を与えたり、大気が反応容器内に流入し反応に悪影響を与えることも防止される。

【図面の簡単な説明】

【図1】本図の(A)は本発明による大気圧プラズマ表面処理装置の1実施例の簡略型の横式縦断面図であり、本図の(B)は標準型を示す。

【図2】図1(B)のA矢視平面図である。

【図3】被処理物体が移動する場合に対処するための第2実施例の縦断面図である。

【図4】被処理物体が繊維状の場合に対処するための第3実施例の縦断面図である。

【図5】図4のA矢視図である。

【図6】被処理物体が繊維状で移動する場合に対処する第4実施例の縦断面図である。

【図7】従来の大気圧プラズマ表面処理装置の概要を示す立面図である。

【図8】図7のA-A断面図である。

【符号の説明】

1、21 反応容器

* 1a、1b、21a、21b 反応容器の側壁

1c 導入口

1d 吹出し口

1e、10e、11e 上壁

1f、11f 側壁

2a、2b 電極

3 電源

5、25 被処理物体

7 グロー放電

10、30 箱体

10a、10b 箱体の側壁

10c、10'c 箱体の吐き出し口

10d、10'd 箱体の吸引口

10f、10'f 箱体の導入口

10g、10'g 箱体の吐き出し口

11、31 外箱体

11a、11b、31a、31b 外箱体の側壁

11c、11'c、31c、31'c 外箱体の導入口

11d、11'd 外箱体の吐き出し口

20 12、32 受箱体

12a、12b、32a、32b 受箱体の側壁

12c 受箱体の吐き出し口

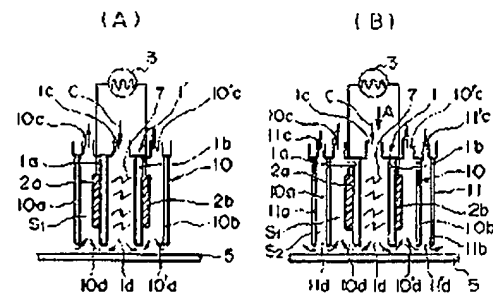
12d 受箱体の吸引口

B、C 矢印

* S₁、S₂ 空間

【図1】

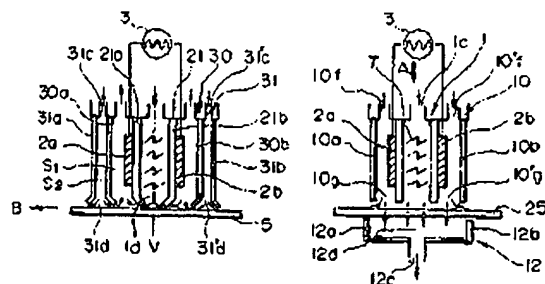
【図2】



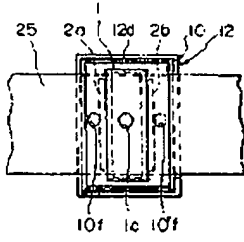
1a、1b: 側壁
1c: 導入口
1d: 吹出し口
2a、2b: 電極
3: 電源
5: 被処理物体
10: 箱体
10a、10b: 側壁
10c、10'c: 吐き出し口
10d、10'd: 吸引口
11: 外箱体
11c、11'c: 導入口

【図3】

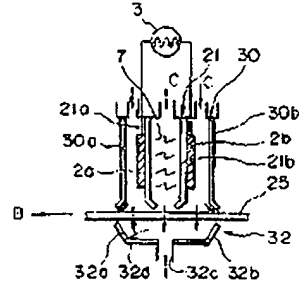
【図4】



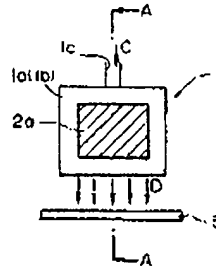
【図5】



【図6】



【図7】



【図8】

